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Triptycene based luminescent metal–organic gels for chemosensing†

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We report a novel luminescent Al-based metal–organic gel G1 comprising 1,4,5,8-triptycenetetracarboxylic acid, which exhibits highly sensitive detection towards nitro aromatic compounds particularly picric acid. Furthermore, under identical reaction conditions, using a Co(II) salt instead, a novel 3D framework material, *trip*-MOF-1, was isolated and its sensitivity towards picric acid was also evaluated.

Design and development of chemosensors for rapid and selective detection of ultra-trace nitroaromatic analytes (explosives), particularly 2,4,6-trinitrotoluene (2,4,6-TNT), 2,4-dinitrotoluene (2,4-DNT), and picric acid (PA), are perceived to be of great importance due to their potential utility in national security screening and also for the environmental concerns.[1] Electron deficient nature of the aforementioned analytes makes them amenable for detection by electron rich fluorescence sensors *via* a photoinduced electron transfer (PET) quenching mechanism.[2] Because the detection sensitivity of the chemosensors is primarily determined by transduction methods,[3,4a–c] design of new materials capable of enhancing the transduction signals, which result from the binding of analyte molecules, is in great demand. Particularly, over the last two decades, Swager and co-workers have pioneered the detection of TNT among other explosives and toxic pollutants using conjugated polymeric (capable of facile long range exciton migration) materials *via* a fluorescence quenching mechanism. Receptors especially based on triptycene derivatives have been successfully employed in the polymer backbone.[1b,4] It has been suggested that incorporation of such rigid 3-D moieties mitigates π-stacking and excimer formation owing to its unique structural motifs while allowing diffusion or hosting of analyte molecules in its geometric void space.[4a,5] Although organic conjugated polymers comprising triptycene have been successfully demonstrated to detect explosives with high sensitivity, to our knowledge, there is no report of triptycene containing metal–organic material used for this purpose. In this contribution, we have sought to investigate the sensing efficiency of the triptycene based coordination polymeric gels,[6] anticipating that the shape-persistent properties of the rigid triptycene unit will remain unaltered. Particularly, we report here a novel synthetic method for the preparation of triptycene based metal–organic gel and its utility as a chemical sensor.

Heating a clear mixture of $Al(NO_3)_3{\cdot}9H_2O$ and 1,4,5,8-triptycenetetracarboxylic acid (H_4ttc)[7] in *N*,*N*-dimethylformamide (DMF) readily yielded an opaque Al-gel material **G1** (Fig. 1a, concluded based on the tube inversion test) within a few hours (see ESI† for details). The FT-IR spectra of the xerogel (Fig. S4, ESI†) clearly showed that the bands due to the carboxylates are shifted to lower frequencies (for example 1693 to 1626 cm^{-1}) with respect to the free ligand. This unambiguously suggests the presence of carboxylate in the metal coordination sphere. Further the gel is not thermoreversible indicating the coordination polymeric nature of the gel network. It is also apparently stable under sealed conditions. However, when open to the air it shrinks markedly over a period of several days. The Al-gel **G1** is also stable when subsequently immersed in various organic solvents such as alcohols, DMSO, DMF and acetone. Microscopic examination of the air-dried gels under a scanning electron microscope (SEM) (Fig. 1c) revealed a sponge-like structure with a disordered arrangement of interconnected macropores in the size range of 50–90 nm.

Dynamic rheology was performed using Al-gel **G1** (overall ~8% DMF gel)[8] to further evaluate its gel-like character. In a typical frequency sweep experiment, the elastic modulus G′ and the viscous modulus G″ were plotted as a function of the angular frequency 'ω' at a constant strain of 0.1%.

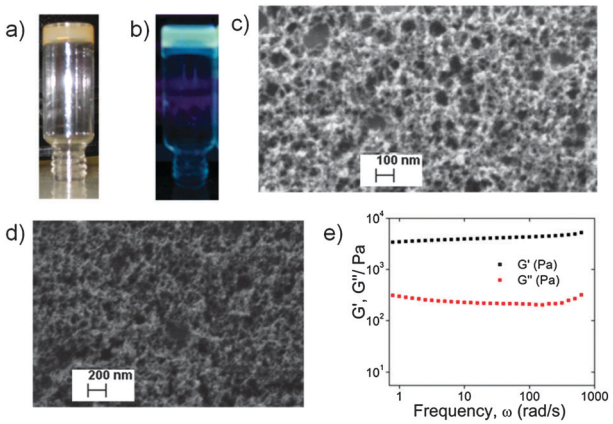

Fig. 1 The photo of as-prepared Al-gel **G1** (a) and Al-gel **G1** under UV lamp (b); the SEM image of the xerogels (air-dried form of as-prepared Al-gel **G1**) (c) and the xerogel prepared from the ethanol dispersed form of as-prepared Al-gel **G1** (d); rheological response of the Al-gel **G1** (e).

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Fig. 1e shows that the G′ values (~4.1 kPa) remained invariant with frequency over a considerable period of the time scale and were significantly higher in magnitude than the corresponding G″ supporting its remarkable gel-like response.

In order to evaluate the scope of the synthetic procedure, other metal precursor salts containing Co(II) and Cr(III) were examined under optimized conditions.[9] Unlike $Al(NO_3)_3 \cdot 9H_2O$, the reaction between $Co(NO_3) \cdot 6H_2O$ and H_4ttc did not result in the formation of gel material, instead allowed the isolation of a crystalline product (designated *trip*-MOF-**1**) of the formula $[Co_2(ttc)(DMF)(H_2O)]$ (*ttc* = 1,4,5,8-triptycene-tetracarboxylate) as established based on single crystal X-ray diffraction (SXRD) and elemental microanalysis.[10] The *trip*-MOF-**1** was further characterized by TGA, FT-IR and powder X-ray diffraction (PXRD) analysis (see ESI† for details). The SXRD analysis revealed that the structure of *trip*-MOF-**1** (Fig. 2a and b) is built up from two Co(II) cations, one *ttc* anion, one metal-coordinated water and DMF solvent molecules. The Co(II) centers are located at special positions with a site-occupancy factor of 0.5. The Co1 atoms lie on two-fold axes while the Co2 atoms lie on centers of inversion. Co1 is tetrahedrally coordinated by four carboxylate oxygen atoms from four different *ttc* ligands and Co2 is octahedrally coordinated by four carboxylate oxygen atoms from two different *ttc* ligands, one oxygen atom from a water molecule and one oxygen atom from a DMF molecule. The *trans* water and DMF ligands are disordered over two sets of sites with an occupancy of 0.5 while the *ttc* ligand is extensively disordered about a crystallographic center of inversion. The Co cations are linked by the *ttc* anions into a three-dimensional framework. Structural analysis of *trip*-MOF-**1** using TOPOS software[11] reveals a 2-nodal 4,6-c net (Fig. 2c) with stoichiometry (4-c)(6-c) and the Schläfli symbol for the net is $\{3^2.8^4\}\{3^4.4^2.8^4.9^4.10\}$.

The tempting light emission from the Al-gel **G1** either in its as-prepared (Fig. 1b) or in the dispersed form in ethanol prompted us to explore its potential application as a chemosensor. Interestingly, no change in the network skeleton was observed when as-prepared Al-gel **G1** was suspended in ethanol (Fig. 1d). The photoluminescence spectra of the ethanol dispersed Al-gel **G1** exhibits strong fluorescence maxima at 385 nm upon excitation at 318 nm,[12] which is red shifted by 10 nm in comparison to the peak at 375 nm (excitation at 315 nm) for the H_4ttc ligand (Fig. S8, ESI†). The fluorescence attenuation of the Al-gel **G1** dispersed in ethanol was investigated using different analytes (quenchers),[13] and the percent (%) quenching is depicted in Fig. 3a. It clearly reveals the varied fluorescence quenching response upon addition of analytes with various degrees of electron deficiency. While an insignificant quenching was observed for nitromethane (NM), chlorobenzene (CB), nitrobenzene (NB) and 1,3-dinitrobenzene (1,3-DNB), a highly efficient quenching was observed for hydroxy substituted nitroarenes *p*-nitrophenol (*p*-NP), 2,4-dinitrophenol (2,4-DNP), 2,6-dinitrophenol (2,6-DNP) and PA. In contrast to the general trend exhibited by the phenolic arenes, *m*-nitrophenol (*m*-NP) however showed low quenching efficiency. This reveals the potentiality for selective detection of 2,4-DNP, 2,6-DNP and *p*-NP over its *m*-substituted analogues. Explaining the trend in selectivity among the hydroxy substituted nitroarenes (*p*-NP, 2,4-DNP, 2,6-DNP and PA); the polarizability and also the π–π interacting ability of the analytes seem to be the most influential. Accordingly, *m*-NP shows lower quenching efficiency as compared to *p*-NP which has greater polarizability.[14] Non-aromatic analytes such as nitromethane also showed a lower quenching response due to the lack of π–π interactions. It is worth mentioning here that, *p*-NP derivatives are also amongst the most toxic pollutants evaluated by US Environmental Protection Agency (EPA).[15] Significantly, Al-gel **G1** showed highest sensitivity towards PA (Fig. 3a) and the limit of detection (LOD) was observed in the range of 5–10 ppb. The fluorescence attenuation of PA and 2,4-DNT (which shows a moderate quenching response) was further evaluated based on the Stern–Volmer plot depicted in Fig. 3b. As expected the Stern–Volmer binding constant, $K_{sv} = 5.3 \times 10^5\ M^{-1}$, obtained for PA was higher than $2.19 \times 10^4\ M^{-1}$ estimated for 2,4-DNT, which evidences a more facile PET from the excited state of the receptor (Al-gel **G1**) to the relatively low lying LUMO orbital of PA (Section S8, ESI†).[1e,3b,16] Incidentally, the K_{sv} ($5.3 \times 10^5\ M^{-1}$) obtained for PA is found to be superior when compared to the other literature known values for fluorescence based chemosensors.[1e,17] Furthermore, when a discrete ligand (H_4ttc) was used as a PA sensor, a significantly low K_{sv} value of $1.2 \times 10^5\ M^{-1}$ was obtained *versus* $5.3 \times 10^5\ M^{-1}$ for the Al-gel **G1**. The improved attenuation response in the case of Al-gel **G1** evidences the impact of the self-assembly of the triptycene receptors into macroporous structures to facilitate long range exciton migration.[18b,e]

In conjunction to the Al-gel **G1** we further evaluated *trip*-MOF-**1**[18] and Cr-gel **G2**[9] as PA sensors (Fig. S24, ESI†). The K_{sv} values obtained for *trip*-MOF-**1** ($5.2 \times 10^4\ M^{-1}$) and Cr-gel **G2** ($4.8 \times 10^4\ M^{-1}$) were however found to be lower

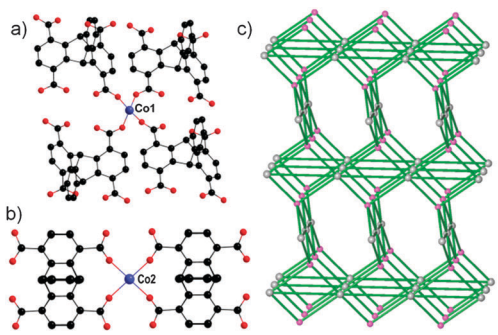

Fig. 2 Partial view of the single X-ray crystal structure of *trip*-MOF-**1**, showing the coordination environment around the metal centers Co1 (a) and Co2 (b) with selected atoms numbered. Atom colors: Co, blue; O, red; C, black. All coordinated solvents and hydrogen atoms are omitted for clarity. (c) Partial view of the 2-nodal 4,6-c net in *trip*-MOF-**1**.

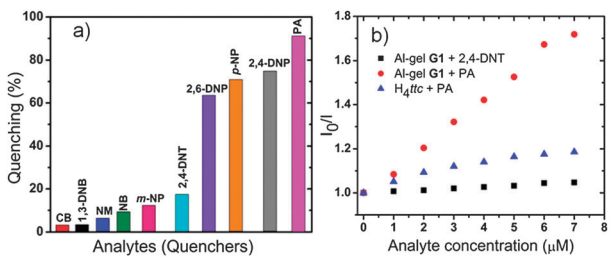

Fig. 3 (a) The percent (%) quenching of the fluorescence of as-prepared Al-gel **G1** dispersed in ethanol by the addition of different analytes (quenchers) at room temperature. (b) The Stern–Volmer plots for the titration of Al-gel **G1** (with DNT, black square and PA, red circle) and H_4ttc (with PA, blue triangle).

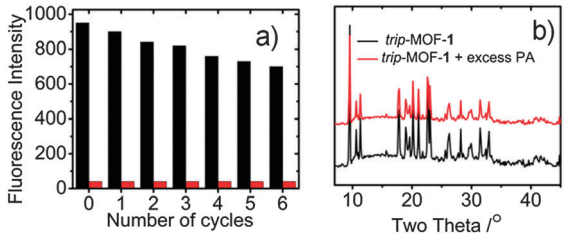

Fig. 4 (a) Reproducibility of the quenching ability of Al-gel **G1** dispersed in ethanol to PA solution. The black bars represent the initial fluorescence intensity and the red bars represent the intensity upon addition of 100 μL (1 mM) of a solution of PA. (b) PXRD pattern of pristine *trip*-MOF-**1** (black) and its ethanol washed material obtained after the treatment with an excess of PA (2 mM) solution in ethanol (red).

than that obtained for Al-gel **G1**. This indicates that the metal–organic material incorporating Al(III) ions has pronounced sensitivity towards PA when compared to Co(II) and Cr(III). The degradation of the coordination network upon addition of acidic analytes such as PA in ethanol could be ruled out by establishing an identical PXRD pattern of pristine *trip*-MOF-**1** and its PA treated material (Fig. 4b).

The sensing ability of the Al-gel **G1** in the solid state when exposed to saturated vapour of various analytes was evaluated (Fig. S26, ESI†). Upon exposure to NB vapour for 6 min, a significant quenching (55%) of the initial intensity was observed. On the other hand, a relatively low quenching (13%) effect was seen in the case of 2,4-DNT and a further diminished response was noted for PA (9%). This is in stark contrast to what was observed in the solution medium. The overall quenching response in the solid state seems to be limited by the relative vapour pressure of the analytes following the order NB > > 2,4-DNT > PA.

The ethanol dispersed Al-gel **G1** could be regenerated and reused for a significant number of cycles by centrifuging the dispersed solution after use and washing several times with ethanol (Fig. 4a and Fig. S25, ESI†). The recovery of the initial emission intensity to a significant extent (~75% after 6 cycles) implies high photostability of the material.

In summary, we have developed luminescent metal–organic materials based on the triptycene receptor for the sensitive detection of nitro aromatic compounds. Particularly, Al-gel **G1** exhibits superior response towards PA. The observed sensitivity could be attributed to the self-assembly of the triptycene receptors into coordination polymeric gel. Such luminescent metal–organic materials can be used as an alternative platform for chemo- and biosensing.

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8 The minimum gelator concentration (MGC) was found to be as low as 1.5 wt% (See Fig. S1, ESI†), however, for better rheological response we chose to use ~8.0 wt% DMF gel.

9 Under optimized reaction conditions Cr(III) yielded a dark-green gel material **G2** confirmed by the tube inversion test (Section S2, ESI†).

10 Microanalysis for *trip*-MOF-**1**, $[Co_2(ttc)(DMF)(H_2O)]$, calcd: C, 51.04; H, 3.01; N, 2.20%. Found: C, 51.52; H, 3.12; N, 2.61%.

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